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LAKE SUPERIOR

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REVIEW OF POTENTIAL PROBLEMS

Organic pollutants may constitute the most widespread waste loadings into the waters of Lake Superior. There are essentially three categories of organic contaminants. The first category consists of those organic compounds that readily degrade biologically or chemically. Visual perturbations are generally detected after degradation because of visible deposition and reduced oxygen levels with subsequent suffocation of some forms of aquatic life (1,2). These reactions can also result in the direct mobilization of metals by complexation (3), conversion of inorganic forms of metals to methyl and dimethyl compounds (4-6), and pH and Eh changes in sediments which may mobilize metals, especially manganese (7) and iron (13).

The second category of organic contaminants is comprised of those which are degraded organic compounds which may be directly toxic to aquatic life and consumers of aquatic life, which may be bioaccumulated in lower levels, which may be metabolized to a more toxic form and stored in higher organisms. An excellent example of such compounds is PCB's which not only directly bioaccumulate to toxic levels but are also metabolized to the more toxic hydroxy PCB's (13).

The third category consists of the many organic compounds that can cause taste and odour problems in domestic water supplies as taste the flesh of food fishes. The best known are phenols (1). Phenols can also combine with chlorine during disinfection and bleaching processes to produce chlorophenols (8) with extremely different properties: generally more basic and susceptible to bioaccumulation, more persistent in the aquatic environment (9), and with strong odours or tastes (9).

Identification of individual organic compounds is difficult in environmental samples, and usually the state of risk is involved. In addition, comparison of data obtained from fish, water, sediment, and birds is often difficult.

The analytical methodology employed for all studies was based on extraction from non-living samples. However, the largest group of potential organic contaminants are those which are not easily extracted from living organisms. These were generally excluded from analysis. An example of this class of compounds is pentachlorophenol which is widely used for preserving wood, especially in aquatic environments. Other inputs to the aquatic environment are polychlorinated biphenyls which are known to be present in detectable concentrations in other areas (10).

Highly stable organic compounds are spread throughout the ecosystem. Little is known about the chemical and biological cycling and fate of these compounds. This is particularly important because of the specific characteristics of Lake Superior, including its very long retention time and the fact that the water from this lake flows into the lower lakes.

The data presented below for specific contaminants are only a representative portion of the data available. More information is found in each of the sections of Chapter 4, especially Chapter 4.1, and in the open water fisheries section, Chapter 5.6. Together, these data unequivocally demonstrate the widespread occurrence of a large number of persistent organic contaminants and the magnitude of the problem associated with these compounds.

SPECIFIC CONTAMINANTS

POLYCHLORINATED BIPHENYLS

PCB's have been recognized as widespread and highly persistent organic contaminants for some years. Their resistance to degradation and lipophilic nature leads to their bioaccumulation and, accordingly, they have been observed in many forms of biota, including man. PCB's in air are found adsorbed onto particulate matter, in snow, and in rain. PCB's present in water accumulate in suspended matter and biota and are either precipitated with sediments or will enter the food chain. Direct toxic effects on aquatic animals, fish, birds, mammals, and man have been noted (1). Because of their widespread occurrence, persistence, bioaccumulation, and toxicological characteristics, U.S. and Canadian agencies have developed objectives and guidelines for maximum PCB levels in water, food, and biota for the protection of ecosystems and of man himself. The current guideline levels are given in Appendix 6. In addition, the Water Quality Objectives Subcommittee of the Water Quality Board has reported (27) that PCB's in water should not exceed 0.001 ug/L but this level may not be adequate to provide protection to certain predators and could not be enforced because of insufficiently sensitive quantification limits.

PCB's were not detected in the waters of Lake Superior at the detection limit of 10 ng/L. However, lakewide contamination is observed in suspension on fishes. All species investigated had PCB residues with the highest levels observed in large size predators, particularly lake trout.

In the offshore fish of Lake Superior, at least in the larger species, higher levels of PCB contamination than in Lake Huron were found. Levels were highest in mature whole lake trout (or salmon) with mean levels of 4.3 ng/kg at Keweenaw Point, 3.7 ng/kg at Elk Bank, and 2.3 ng/kg at Copper Harbor. In other species (bluntnose chub, burbot, lake herring, and slimy sculpin) levels ranged up to 2 ng/kg and were low only in those slimy sculpin which were small and obviously very young fish. Analysis for two samples of whole and fillet portions of lake trout from the Apostle Islands showed 1.00 and 1.00 ng/kg for whole and fillet fish, respectively.

Detailed investigations were undertaken on sampling sites along the northern shore, from Pine Bay to Batchawana Bay (14). PCB residues in edible portions of fish, on a wet weight basis, were found to be in the order of 0.3 mg/kg in whitefish, 0.6 mg/kg in lake trout, and 0.5 mg/kg in lake herring, respectively. In Lake Superior waters north and east of the Apostle Islands (15) mean PCB residues were 30.7 mg/kg in chub, in lake herring, and in whitefish. The same survey observed PCB levels of 32.0 mg/kg in lake trout 41.5 kg weight, and a mean 34.0 mg/kg in lake trout 22.5 kg weight.

Fish such as herring, herring, yellow perch, whitefish, brook trout, white sucker, mottled sculpin, and muskellunge in waters between Duluth and Pine Bay (16) were found to contain PCB residues in the range of 0.2 to 0.5 mg/kg in edible portions on a wet weight basis. In the same area, lake trout, chub, water cisco, deep water cisco, and long nose sucker had PCB mean residues of 31.0 mg/kg in edible portions. A survey near Dock Harbour, Lake Huron, and off Georgian Island (17) indicated PCB contamination in a range of 2.7 to 13.8 mg/kg in edible portions of lake trout. Mean PCB concentrations exceeded the U.S. Food and Drug Administration (FDA) guideline of 3.0 mg/kg for fillets of lake trout from Hamilton (3.10 mg/kg), Marquette (5.0 mg/kg), and Black River (8.37 mg/kg). Lake trout from these locations averaged 5.33 mg/kg whitefish and herring averaged 0.54 mg/kg. Additional data are given in Chapter 5.4.

Lake trout from most areas of Lake Superior are contaminated with PCB's close to or in excess of the Canada health protection guideline of 3.0 mg/kg in fish. This is particularly evident in large lake trout which may have PCB levels several times this value and hence are also exceeding the U.S. FDA guideline of 3.0 mg/kg in edible portions of fish.

Although PCB input into the Great Lakes is definitely associated with industrial and municipal effluents (Chapter 3.2) (18, 19), total loadings from these sources and from tributaries do not account for the PCB residues observed in the sediments and the biota of these waters, nor for the widespread and generally uniform PCB distribution. From a very limited investigation on PCB's in rain (10) it is known that PCB's may be present in precipitation; the observed concentrations of less than or near 0.02 µg/l (including particulate fallout) may account for an input of 1,000 kg/a to Lake Superior.

The ecological impact of chlorinated hydrocarbon compounds has severely affected the fishery of Lake Superior. Continued inputs of PCB's may entirely eliminate the use of fish as a food source. Immediate and decisive steps must be taken to prevent further contamination and degradation.

DDT AND ITS METABOLITES

DDT and its metabolites (DDD and DDE) were the first of the general group of compounds known as chlorinated hydrocarbon insecticides to receive worldwide attention as a highly persistent contaminant present in practically all trophic levels of the environment. DDT's are particularly known for their bioaccumulation characteristics in aquatic organisms, their effects on fish and wildlife, and their potential carcinogenicity to humans. Reported

as present in fishes of the Great Lakes during the mid-1960's (20), DDT was banned from use in the states bordering on Lake Michigan during 1969-70, essentially banned in Canada in 1970, and banned in the entire United States in 1972. Since the control on DDT usage by the states bordering on Lake Michigan, average residues of this insecticide have declined dramatically in that lake (21) and in the lower lakes in general. Current recommended guidelines or criteria for maximum allowable concentrations of DDT in water and the aquatic biota are given in Appendix G.

Residues of DDT and its metabolites were present in essentially all samples of fish from Lake Superior. Mean values ranged from 0.01 $\mu\text{g/g}$ in bullheads (fillets) from the mouth of the Bad River to a high of 8.17 $\mu\text{g/g}$ in lake trout (whole fish) off Coppermine Bank. Obvious differences were noted between concentrations of DDT residues found in fillets of lake trout versus whole fish. Based on samples taken at the Apostle Islands and in the vicinity of Isle Royale, it would appear that the average total DDT concentration was between 2 and 4 times higher in whole fish than fillets. The question of comparability between whole fish and fillet analysis remains, however, essentially unresolved because of the differences in size, fat content, and possible population difference in the fish sampled.

Of the fish taken as part of the Michigan nearshore program, the mean DDT concentration exceeded the 5.0 $\mu\text{g/g}$ U.S. FDA guideline in edible fish tissues only in far lake trout from Black River Harbor (5.1 $\mu\text{g/g}$). Concentrations in excess of the guideline were occasionally found in the edible portions of individual fish from Lower Portage Entry, Copper Harbor, Marquette, and Munising. The highest value (26.02 $\mu\text{g/g}$) was in a lake trout from Munising. About half the lake trout exceeded the proposed Agreement objective of 1.0 $\mu\text{g/g}$ in whole fish. The average total DDT concentration in lean lake trout was 2.03 $\mu\text{g/g}$ and the average concentration for herring and whitefish in Michigan nearshore waters was 0.50 $\mu\text{g/g}$. Additional data on DDT in nearshore fish are given in Chapter A-1.

Mean levels of total DDT exceeded 5.0 $\mu\text{g/g}$ in mature whole lake trout from Batoua Beach, Keweenaw Point, and Coppermine Bank. All remaining lake trout samples contained DDT in excess of 1.0 $\mu\text{g/g}$. Historically, all samples of bloater chubs contained average DDT residues in excess of 1.0 $\mu\text{g/g}$ except for those from Whitefish Point (0.87 $\mu\text{g/g}$). Of the remaining species analyzed (burbot, herring, and slimy sculpin), only burbot showed DDT residues over 1.0 $\mu\text{g/g}$.

All sediment samples from Black Bay contained trace levels (1.0 $\mu\text{g/kg}$) of DDT, DDD, and DDE. Lake trout from Black Bay had a mean DDT concentration of 0.960 $\mu\text{g/g}$.

Although the data suggest that occasional lake trout from Lake Superior will exceed the food guideline of 5.0 $\mu\text{g/g}$, the vast majority of fish caught are below the U.S. FDA and Canada health protection guidelines for DDT in fish. However, several species of fish exceed the proposed Agreement objective of 1.0 $\mu\text{g/g}$ whole fish for the protection of fish and wildlife. It also appears that average values of DDT in Lake Superior fish have not declined

from those levels previously reported (15,17,20). The oligotrophic characteristics of Lake Superior and/or possible continued sources of DDT to the lake are the only reasonable explanations for the failure of DDT residues to decline. If continued sources of this compound are causing the residue levels to remain high, then monitoring should be continued to locate and possibly eliminate the contamination. Possibly the chemistry of the water case itself is responsible for the detection of isomers of DDT, particularly DDE, in the system.

ALDRIN PLUS DIELDRIN

Aldrin is metabolically converted to dieldrin by aquatic organisms and by direct oxidation. Dieldrin is considered to be as toxic or slightly more toxic than aldrin to aquatic organisms. Further, it is highly persistent, bioaccumulatable, and a potential human carcinogen. Because of these adverse features, the U.S. Environmental Protection Agency (EPA) suspended the production and use of both aldrin and dieldrin in 1976. Dieldrin was first reported as present in fishes of the Great Lakes in the late 1960's (20) and routine evaluation of dieldrin levels in lake Michigan fish since 1969 by the U.S. Fish and Wildlife Service has shown no significant change in average residue levels (21). Guidelines or criteria for maximum allowable concentrations of aldrin and/or dieldrin in water and the aquatic biota are given in Appendix B.

Concentrations of dieldrin in nearshore fish (fillets) ranged from none detected to 0.12 $\mu\text{g/g}$. Of the results reported, approximately one third were as none detected or only trace amounts of dieldrin.

In whole fish collected as part of the offshore program, dieldrin residues ranged from 0.1 to 0.47 $\mu\text{g/g}$. The highest value (0.47 $\mu\text{g/g}$) occurred in coho salmon taken from the Apostle Islands region. However, fillets of lake trout from the same area contained an average of only 0.21 $\mu\text{g/g}$ dieldrin. Similarly, whole lake trout from Bateman Rock contained 0.32 $\mu\text{g/g}$ while fillets of lake trout from nearby Isle Royale contained no detectable dieldrin residues. These limited data suggest that dieldrin can be expected to be lower in the edible portion of the fish than in whole fish. Nevertheless, dieldrin residues of 0.47 $\mu\text{g/g}$ in whole lake trout and 0.21 $\mu\text{g/g}$ in lake trout fillets from the Apostle Island region is of concern since whole herring chubs from the same area contained 0.33 $\mu\text{g/g}$. These values were considerably higher than those found at any of the other stations in the lake.

Bainest (20) reported dieldrin residues ranging from 0.01 to 0.05 $\mu\text{g/g}$ in a variety of fish species (whole fish) collected from Lake Superior in 1967-68. Analysis of the edible portions of lake trout from Thunder Bay showed a mean of 0.055 $\mu\text{g/g}$ unperfished and having contained 0.059 $\mu\text{g/g}$ and 0.020 $\mu\text{g/g}$, respectively. Additional data are given in chapter 4.1.

While dieldrin residues were found to exceed the U.S. EPA guideline of 0.3 $\mu\text{g/g}$ in edible portions of fish, elevated levels of dieldrin approaching 0.3 $\mu\text{g/g}$ were detected in the Apostle Islands region. Because of this and the persistence of this compound at concentrations equal to or greater than

levels reported in 1967-68, additional monitoring of tissue burdens is needed. The effects of this compound on the ecosystem have not been assessed and should be studied.

HEXACHLOROBENZENE

Hexachlorobenzene was found in nearshore and offshore fish in the concentration range of 0.001-0.1 µg/g in both Canadian and U.S. waters (16,22). Analyses in water and effluents were not performed or were reported as less than detection limits depending upon the methodology employed.

No safe levels have been established in water or tissue for this compound; however, insignificant bioactivity is known. Data indicate the conversion to pentachlorobenzene, a universally accepted weak preservative, as a fungicide, and in the manufacture of rubber for tires and other chemicals (24).

The ecological significance of this widespread non-degradable compound should be determined. Concentrations in effluents, water, and biota should be monitored to determine sources and possible effects on aquatic life. Safe levels should be established in food containing this compound, since its presence is now known but the associated hazard is not.

LINDANE

The γ -isomer of lindane is the active component in hexachlorocyclohexane. Trace quantities have been found in fish and water but levels are well within the proposed agreement objective of 0.3 µg/g in edible portions of fish and 0.01 µg/l in water (see Appendix C). In addition, trace amounts (up to 0.035 µg/l) of lindane were found in every water sample examined (24,26).

Mature whole lake trout and chin from Coppermine beach had a mean of 0.2 µg/g and 0.317 µg/g, respectively (22). Trout from the Apostle Islands had a level of 0.05 µg/g for mature whole fish compared to 0.03 µg/g in fillets (23). The values reported are for hexachlorocyclohexane and include γ -lindane. For nearshore fish, levels (16) in fish tissue were all well within the proposed Agreement objective; the concentration was 0.005 µg/g in almost all of the nearshore fish sampled.

Because of the extreme persistence of this compound and its continued use, continued monitoring in fish and fish-consuming animals is needed. The potential effects of lindane are unstudied in Lake Superior and efforts should be made to determine the significance of widespread observations of trace levels.

CHLORDANE

Technical grade chlordane is a mixture of different isomers of which the α and γ -isomers represent 82% each. These two isomers, both persistent, are reported frequently as "chlordane," either separately or collectively, in environmental samples together with smaller amounts of nonchlorine isomers and the metabolite oxychlordane. The use of this preparation is not restricted in the United States although it is permitted for limited agricultural use in Canada.

Movement from soil into aquatic ecosystems by surface runoff or ground water has been affirmed (28,29); these substances may also enter the aquatic ecosystem in precipitation, a pathway observed for other organochlorines (10).

Nearshore data for whitefish, lake trout, and herring from Ontario waters (15) were sparse, the weighted mean being 0.5 µg/kg in edible portions on a wet weight basis. Herring Bay lake trout were observed to have higher levels (15.5 µg/kg) as were herring (11.9 µg/kg). In addition, other samples in Thunder Bay were found to contain 14.6 µg/kg, but this is not directly comparable with other values since they were done on a whole fish basis, and replication of samples indicated a larger variation in levels.

Samples of offshore fish (22) were obtained in the vicinity of the Apostle Islands and Copper Harbor Point Bank. There were no significant differences between analyzed levels observed in herring (0.18 µg/g) and haddock (0.21 µg/g) from the two areas. The levels were somewhat higher (0.35 µg/g) for lake trout taken in the Apostle Islands area and lower (0.06 µg/g) for other samples from the same region.

The observed levels are of course, sources must be identified.

METHOXYCHLOR

Methoxychlor is used for the control of agricultural pests and of biting insects. This compound may be lost to the environment by volatilization; it does not readily leach from soils (30). The proposed Agreement objective is 0.050 µg/l for the preservation of aquatic life. This level has not been achieved in Lake Superior possibly as a result of degradation to less persistent metabolites and loss to the sediments. Methoxychlor has been looked for (25) but not found in any of the water, sediment, or sediment samples (quantitative limits 0.01 µg/l, 50 µg/kg, and 0.01 µg/kg, respectively) in Lake Superior. Extraction of fish samples (fillet portions) at the Upper Lakes has been made for methoxychlor (11), but it was not detected at levels above 2 µg/kg. It is, therefore, not considered to be a problem in this area. In offshore fish of both lakes, 50.5 µg/kg was found in all samples (whole fish).

Continued monitoring in water and fish are needed as usage of this material increases, especially in high application areas.

POLYNUCLEAR AROMATIC HYDROCARBONS

The polynuclear aromatic hydrocarbons naphthalene, methylanthracene, phenanthrene, and methylphenanthrene have been found in the approximate range of 0.01-0.5 µg/g, total, in offshore fish samples from both U.S. and Canadian sampling stations (27). Polynuclear aromatic hydrocarbons are known to be often present in industrial effluents containing oil and grease. Large loadings of both oil and grease in water have been reported as a result of man's activities (18,19), and these compounds have been identified in effluents from petroleum refining, coal processing, and coke manufacture (23). These compounds may be expected to be decomposed by other, more toxic desirable polynuclear aromatic hydrocarbons.

No safe levels for these compounds have been determined in fish tissues but maximum levels for the protection of aquatic life are 0.01 mg/l total hydrocarbons and for domestic water supply to be "virtually free" from oil and grease. In addition, polynuclear aromatic hydrocarbons have been demonstrated as carcinogenic in test animals at relatively high exposure levels.

This class of compounds should be measured in effluents and aquatic biota to determine exposure, and possible effects on fish-consuming animals, including man, should be investigated. Since their presence has now been discovered, in food, safe levels should be established for human consumption.

CHLOROBENZENE COMPOUNDS

Tri-, tetra-, and pentachlorobenzenes were found in offshore fish from Ontario (22) in total concentrations of 50.01 to 0.5 ug/g. No safe levels have been established in water or food for chlorobenzenes. Their uses include solvents for high-voltage electricals such as dyes and insecticides (spray preparations) and as lubricants and heat transfer media (24).

These compounds are very persistent and in view of their widespread use and resulting fish contamination, they should be monitored to determine sources and possible effects on aquatic life and consumers of aquatic life, including man. Since they have been detected in food, safe levels should be established for human consumption.

PHENOLS

Phenol and other compounds that can cause taste and odor problems have been measured in many effluents discharging in the lake and have been found at levels exceeding water quality criteria particularly at Georgian Bay and nearshore areas adjacent to Huron (25), Georgian Bay (26), Jackfish Bay (27), Thunder Bay, and Dutch-Frontier Harbor. The proposed Agency objectives and the water quality criteria are 0.001 mg/l to protect domestic water supplies and to minimize fish poisoning (see Appendix C).

Phenols are biodegradable; however, if they are present in water during distillation or bleaching processes, they may form chlorinated compounds (8). These compounds are much less degradable, are toxic to bacteria and other aquatic life, have greater potential for bioaccumulation (9), and are more objectionable in taste and odor problems. The polychlorinated compounds may form carcinogenic due to methylated groups of some bacterial strains (39) and are detectable in water and fish tissue at very low levels (39).

Proper treatment of wastes containing these compounds before chlorination will eliminate both taste and odor problems in domestic water supplies and fish poisoning problems. Bleaching processes using chlorine pose a special problem. Monitoring of effluents for the polychlorinated phenols and related compounds should be done routinely. In view of the magnitude of the wastes which contain phenols, analysis of these compounds and their chlorinated derivatives in fish tissue should be undertaken to determine the extent to which the biota may be contaminated.

PHTHALATE ESTERS

Phthalate esters are extensively employed as plasticizers in plastic manufacturing and processing. Recently, phthalates have been detected in many industrial and municipal discharges in the Great Lakes (33) area ranging as high as 1.2 mg/l. Phthalates have been detected in settleable solids at levels as high as 75 mg/l (dry weight). It is likely that these values represent a minimum level (excluding contamination) since they can meet as emulgators (34) which are not likely to be extracted by normal analytical techniques. These esters may be readily eliminated on exposure to clean waters (35). Chronic toxicity considerations (36) resulted in proposed Action Limit objectives of 1.0 mg/l for dibutyl phthalate, 0.8 mg/l for di(2-ethylhexyl)phthalate, and 0.3 mg/l for other phthalate esters for the protection of aquatic life; these levels are only slightly above the analytical capabilities of monitoring laboratories.

Phthalates are noted (37) in nearshore and offshore waters of the Great Lakes. In Minnesota nearshore waters, dibutyl phthalate was measured in whitefish, skinless fillets of Atlantic lake trout, and chinook fillets of brook trout at 2.8, 1.9, and 0.1 mg/kg, respectively. Dibutyl phthalates were found in rainbow trout (0.4 mg/kg) and lung in muskies (0.1 mg/kg). The highest level of diethylhexyl phthalate was observed in whitefish fillets of about 12.5 mg/kg. Phthalates are accumulating in Great Lakes fish, notably lake herring fish where levels are in the range of 8-10 mg/kg and 18-20 mg/kg in selected species (38). See Chapter 4.1 for additional discussion. Since phthalates cannot as yet be associated with deleterious effects, they are not considered to be a major problem. They should, however, be monitored in waters receiving municipal and industrial discharges until such time as feeding experiments can establish no-effect levels.

CHLOROPARAFFIN

Chloroparaffins and related compounds similar to those in toxaphene were identified in near lake fish species from both O.R. and Wisconsin sampling stations at concentration levels in the concentration range 0.1-1.0 mg/g (39). The presence of similar compounds has been established in water adjacent to and downstream of a kraft pulp mill effluent (38).

No safe levels have been determined in food or for fish-consuming animals. Because of the observed levels in open lake fish and the fact that direct sources of these compounds are at this time undetermined, monitoring of these compounds in effluents and aquatic life is recommended.

DECHLOROSTYRENE

Dechlorostyrene was found in fish from Lakes Huron, Ontario, and Michigan (22,36). This compound has not been found in lake superior fish. From open waters and analysis were not made for this compound nearshore fish.

No safe level has been established for the compound. The only previous reports of the compound come from Europe (32). Sources of this compound are not generally known but it is a suspected byproduct in the manufacture of polychlorinated biphenyls (36).

Because of its apparent inertness and ability to bioaccumulate, this compound should be studied to determine if there are effects on Lake Superior and pass effects on the biota. Consideration should be given to establishing criteria for food products.

METHYLBENZOTHIOPHENE

Methylbenzothiophene has been found in fish from the open waters of Lake Huron but not in Lake Superior fish. No safe levels have been established for the compound in fish or water. Benzothiophene is a contaminant in coal products and will leach from coal processing residues (25). Sources and bioactivity of this compound should be investigated as it is a probable future candidate for contamination of Lake Superior fish.

BIPHENYL

Biphenyl was not found in Lake Superior fish but was found in offshore fish from Godwin, Ontario and is known to be often present in industrial effluents containing oil and grease. Large loadings of both oil and grease in water have been computed as a result of man's activities (18,19), and this compound has been identified in effluents from petroleum refining, coal processing, and coke manufacture (24). Biphenyl mixtures may be expected to be accompanied by other, even less desirable polynuclear aromatic hydrocarbons.

No safe levels of these compounds have been determined in fish tissue but criteria for the protection of aquatic life are 0.01 mg/l total hydrocarbons. Criteria for domestic water supply indicate that the water supply should be "virtually free" from oil and grease.

Biphenyl is used as a dye carrier in the textile industry and may be present from oil refining or coal processing. Possible occurrence in chlorinated water supplies or municipal wastes could result in the formation of chlorobiphenyl as a result of disinfection (9).

Biphenyl should be monitored in effluents and aquatic biota to determine sources, and possible effects on fish-consuming animals, including man, should be investigated.

ENDOSULFAN

Endosulfan is employed extensively as an agricultural pesticide and it may be present in agricultural runoff for short periods (1-2 weeks) after application (11). In addition to runoff, it is possible that aerial deposition may introduce this compound into the surface waters of the Great Lakes (10) presumably both to nearshore areas and the open lake. However, under the aerobic, slightly alkaline conditions normally observed in Lake Superior, it is not expected to persist but rather to degrade at least in either the endosulfan sulfate (12) or diol (11). These compounds have not been reported in organisms of Lake Superior. Consequently, no identifiable problem is associated with the use of endosulfan. It should be noted that the residues

tions for these three compounds have not been extensive and receiving waters of agricultural drainage should be examined more thoroughly.

These compounds have not been observed in any water, tissue, or sediment samples in Lake Superior (23) above levels of 0.01 $\mu\text{g/L}$, 30.2 $\mu\text{g/g}$, and 0.01 $\mu\text{g/g}$, respectively; however, because of the high toxicity, monitoring is suggested in areas where this compound is used and studies should be initiated to determine breakdown products and metabolites in the Great Lakes.

CYANIDE

Cyanide is used widely in metal plating, treating, and mining. Waste loadings to Lake Superior are reported as 41,300 kg/d (10,12). Little or no data are available to determine the possible effects of the cyanide loading on the lake ecosystem and studies are needed to determine if other than localized effects have occurred.

HEPTACHLOR EPOXIDE

The proposed Assessment objective for heptachlor plus heptachlor epoxide in the edible portions of the fish is 0.3 $\mu\text{g/g}$ for the protection of human consumers of fish (1,21 see Appendix C). Heptachlor epoxide is found in concentrations of 0.001 to 0.010 $\mu\text{g/g}$ in a variety of fish and fish tissues in Lake Superior (22). Although analysis of edible portions of fish indicate concentrations lower than present guideline levels, continued monitoring of this persistent chemical is needed to determine sources and residue levels satisfactory for human consumption.

OTHER ORGANIC CONSTITUENTS

A wide range of other organic constituents found in whole-fish samples of lake trout from Coppermine Bay and the Apostle Islands is given in Table 3.6-13. Several of these are new in reports of Great Lakes contaminants. Of greatest concern is the fact that many of these compounds are noted for their stable characteristics and long lives in aquatic systems. They can only be attributed to products of man and his activities. Too little is known regarding chronic effects to permit any estimate of the direct risk to fish stock or to wildlife and man as a consumer of this low level contamination. Still less is known of the pathways by which they reach fish and the effects which they may have on other components of the aquatic ecosystem and hence indirectly on fish.

DISCUSSION

All organic contaminants have the potential to adversely affect aquatic resources by either reducing the survival, growth, and reproduction of fish and fish food organisms or contaminating the water and/or fisheries of Lake Superior unfit or unsafe for consumption by higher life forms.

PERSISTENT ORGANIC CONTAMINANTS

The dispersion of persistent organic contaminants throughout the Lake Superior ecosystem occurs both within the lake and through atmospheric transport. Whole-lake degradation is clearly indicated. Atmospheric inputs appear to be a significant source since several of the compounds were found at comparable levels in both Lake Superior and Lake Huron. Further evidence of atmospheric transport is indicated by the presence of similar concentrations of such persistent organic compounds as PCB's, hexachlorobenzene, heptachlor epoxide, and methoxychlor in fish from Lake Superior and in fish from Winnetit Lake, an inland lake on Lake Superior which has received no known direct discharges of these compounds.

Regardless of the absolute concentrations of this wide array of chlorinated hydrocarbons found in water and biota of the Upper lakes, the Reference Group is concerned over the known presence of numerous toxic organics whose individual effects, acute or chronic, toxic or sublethal, are poorly known and whose potential combined effects are completely unknown both in the aquatic biota and in organisms which depend on them for food. It is apparent that Lake Superior is being contaminated with persistent toxic organic compounds from essentially unknown sources. Past efforts to control POP contamination, although effective in Lake Michigan, appear to have had little effect as yet in Lake Superior. Further contamination of the biota by PCB's and, to a lesser degree dieldrin is still considered unavoidable in the Upper lakes. There is also a real potential that if pollution by toxic organics continues unchecked, the fisheries may eventually be lost because of public health problems or, in the extreme, actual loss of the resource from the lakes. This evidence indicates apparent ineffectiveness of controlling toxic organics through partial bans. The only answer is total bans.

TASTE AND ODOR COMPOUNDS

Excessive levels of taste and odor causing compounds are traceable to pulp and paper mills at Marathon, Thunder Bay, Nipigon Bay, and Jacobus Bay, and to several industries in the Duluth-Superior Harbor area. It is expected that ongoing or planned remedial programs at the Sault Ste. Marie mill at Red Rock (Nipigon Bay) and the Great Lakes Paper Company mill at Thunder Bay will reduce present discharges of taste and odor causing compounds to levels in compliance with Agreement and Ontario objectives, but it will be necessary to take additional measures to abate the problems originating from the remaining pulp and paper mills. The technology is presently available to achieve this abatement.

CONCLUSIONS

The Reference Group concludes that a total ban should be implemented on the manufacture, sale, transport, and use of CH's, aldrin, dieldrin, and DDT and its derivatives. For other man-made organics such as halogenated hydrocarbons, an accelerated program is required to evaluate effects on human health and biota, to establish a better basis for criteria, and to develop remedial programs as needed. Until the effects are fully understood, there

should be no increased manufacture, use or discharge of these compounds. Further, before new organic compounds are produced, distributed, or used, environmental and health effects should be fully evaluated. Programs to minimize pesticide use should also be implemented. In addition, remedial measures should be undertaken to eliminate the toxic and odour problems.

CHAPTER 6.4

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